Proposed vibrational mode to explain negative thermal expansion in ZrW_2O_8

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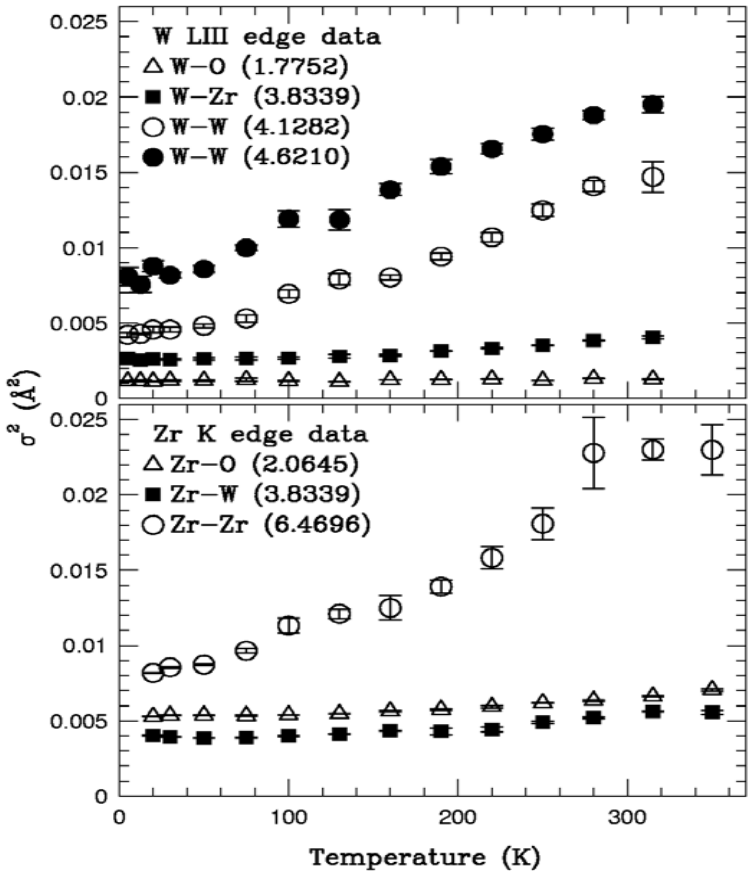
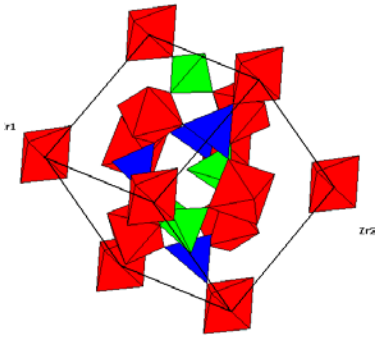
Background

- ZrW_2O_8 contracts when heated from 10-1000K (A negative thermal expansion). Why?
- The crystal is formed of WO_4 tetrahedra (Green and Blue) and ZrO_6 octahedra (Orange) connected at corners, with one corner of each WO_4, unconstrained. This corner is on a cube diagonal. The crystal structure is open.

Data

- Use X-ray absorption fine structure (XAFS) to measure the width, σ^2, of the pair distribution function for various pairs of neighbors.
- σ^2 for W-O and Zr-O neighbors has a weak T-dependence (open triangles). This indicates that the WO_4 tetrahedra and ZrO_6 octahedra are rigid units.
- Surprisingly, σ^2 for W-Zr (or Zr-W) also has a weak T-dependence (solid squares) which indicates that the W-Zr linkage is also very stiff.
- σ^2 for the W-W and Zr-Zr pairs increases rapidly with T.





New Result

Displacements of W, O and Zr atoms are highly correlated.

Combining σ^2 with the thermal parameters, U, from diffraction, allows us to determine the correlations in the displacements of various atoms in the system. The large Ul parameter for W, O and Zr atoms and the small temperature dependence of σ^2 for the W-O, Zr-O, and W-Zr pairs suggest that the motions of W, O and Zr atoms are all highly correlated.

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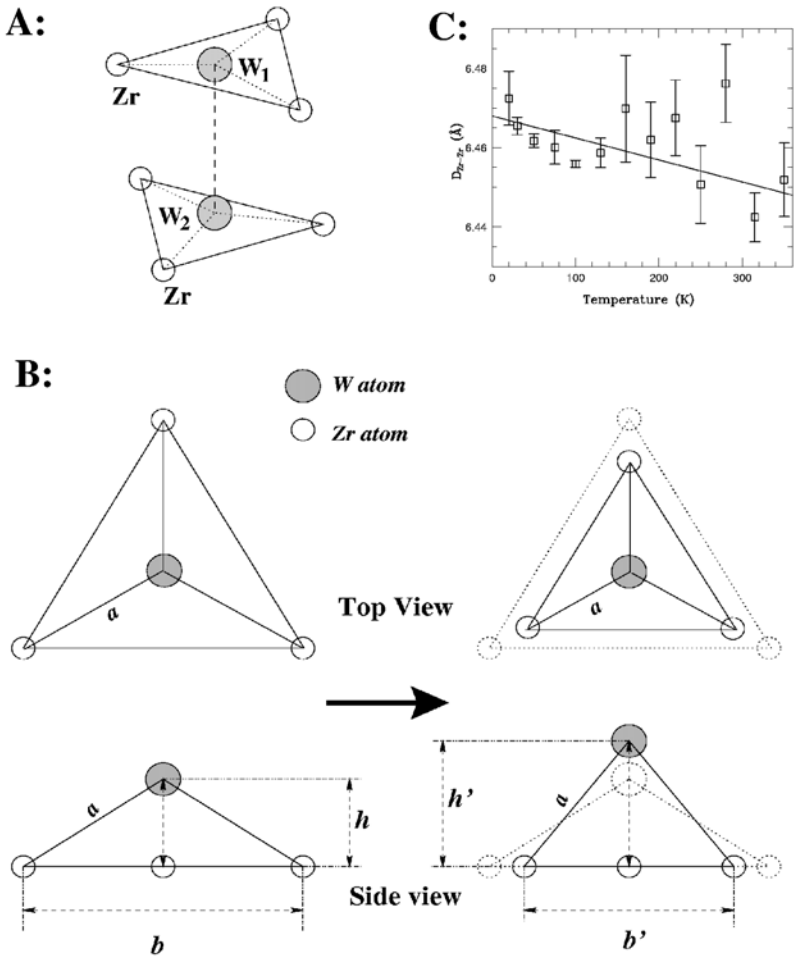
Model

- W (W_1 and W_2) vibrates vertically within triangle of Zr, along unconstrained direction. (See A and B)
- If W-Zr length (a) is fixed, Zr-Zr must contract (b goes to b') as W vibrates above (or below) plane of Zr (See B). Since the Zr atoms form the frame of the unit cell, the entire crystal contracts as the vibration amplitude increases with T.

Broader implications

- Clusters of atoms (WO_4, ZrO_6) clearly move as a rigid unit (RU). The motions of different RU's are correlated.
- An open crystal structure with some atoms unconstrained leads to novel vibrations of RU's, which are not observed in simple systems. May also be present in other complex structures.
- Potential practical applications - combine ZrW_2O_8, (or other negative expansion material), with other materials to make a composite that does not expand or contract with T.



Educational

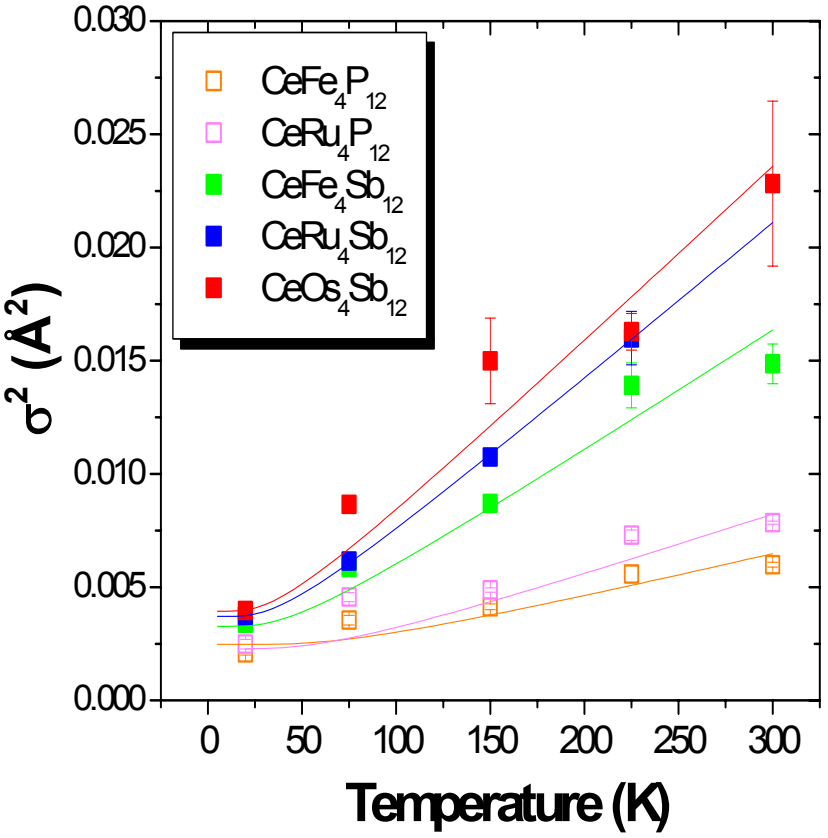
- Daliang Cao (Graduate student) - this work is part of his thesis project. Trained to use XAFS technique and run experiments at a Synchrotron source. Undergraduates helped collect data.

EXAFS results for Ce in the filled Skutterudites
Frank Bridges, UCSC, , DMR Award DMR-0071863

•The XAFS measurements on the Ce L_{III} edge show that the σ^2 *vs.* T curve can be fit well to an Einstein vibrational model. The low Einstein temperatures – from 80-150K -confirms that the filler Ce ions are "rattlers" which scatter phonons to reduce the lattice thermal conductivity.

•Because the data can be fit with very small static distortion- and σ^2 is small at low T, the Ce atom is most likely on center.

• The rattling amplitude is inversely proportional to the Einstein temperature, and increases with the lattice constant of the material.



XANES results for three Eu filled antimonide skutterudites
Frank Bridges, UCSC, , DMR Award DMR-0071863

•The Eu L_{III}-edge XANES data for three Eu filled antimonides are shown in the plot. The XANES results indicate that the local electronic environment about Eu for these three materials is nearly identical.

•Comparison with other Eu^{2+} and Eu^{3+} standards suggests that Eu in these three materials are mainly Eu^{2+}.

•Although the Eu behaves similarly for the three materials, the magnetic properties differs significantly for $EuFe_4Sb_{12}$: the saturated magnetization is just 50% of the other two materials and T_C is more than 10 times higher. Therefore the Fe atoms in this material must play a role in the sample's magnetism.

Brief summary of outreach activities:

Educational:
1 undergraduate, Paul Chesler
1 grad student, Daliang Cao